Development of a geochemical code to assess cement reactivity

Bruno Huet, Richard Fuller,
Jean Prevost, George Scherer
(Princeton University)
Collaborator: Jim Johnson (LLNL)

Introduction

Objective of our work:

Assess the reliability of the CO_2 storage with time.

1. Reliability of geological formation limited by the presence of engineered high permeability path (well bores).

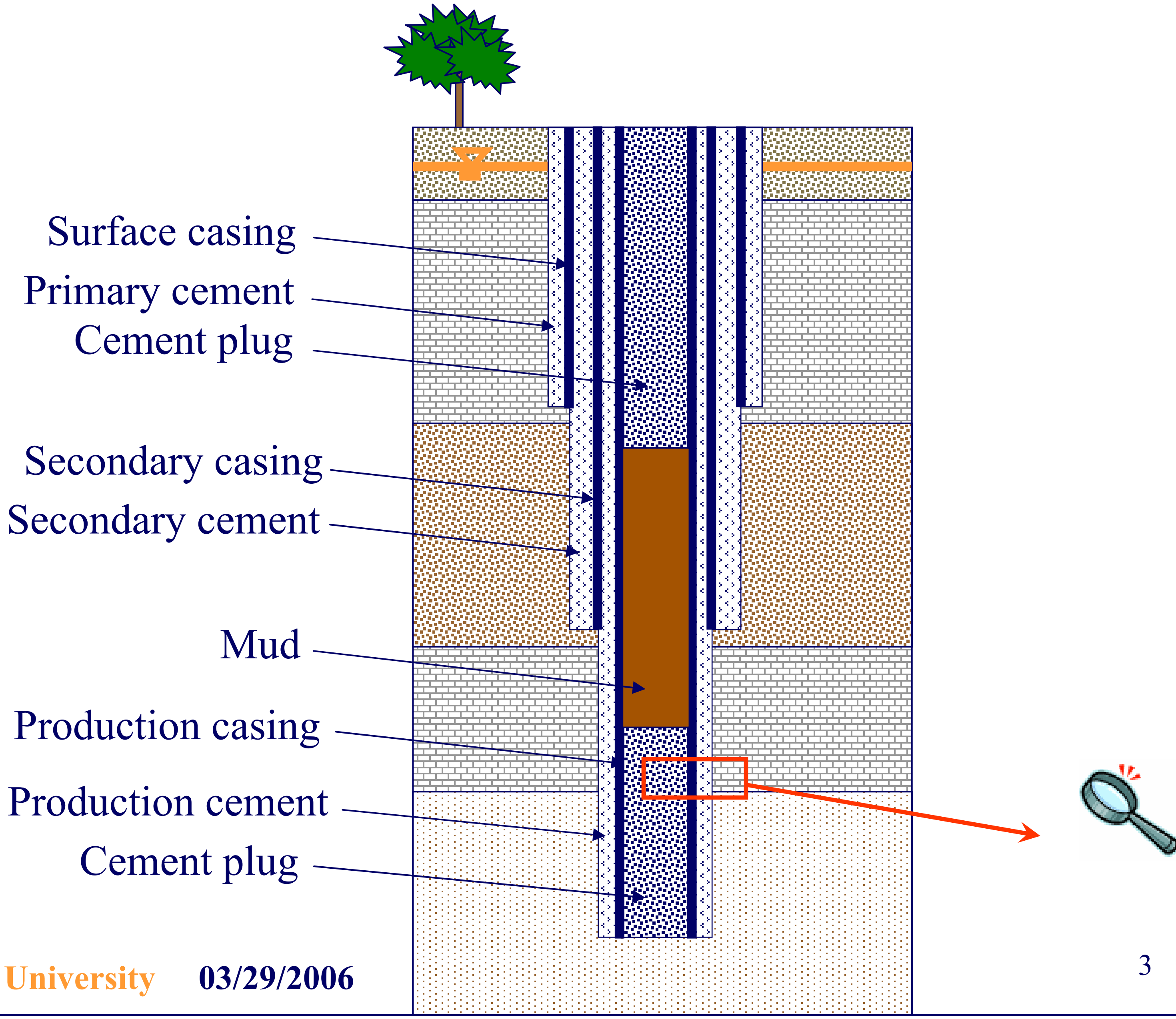
2. Degradation of casing materials (steel, cement) may increase the CO_2 leak with time.

Coupled modeling and experimental approach

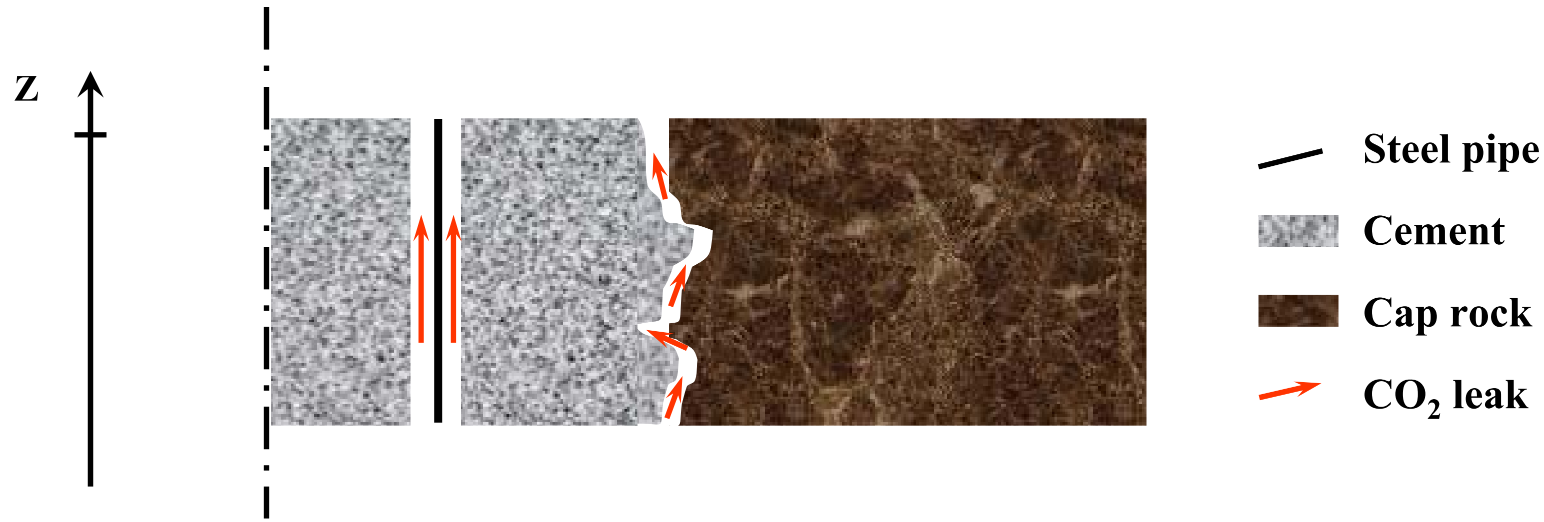
Modeling approach:

1. Aqueous chemistry
2. Transport processes

Sketch of a typical abandoned oil well



Possible CO_2 leaks along high-permeability path



Three main mechanisms (P, T dependent):

1. Multiphase transport within annulus: aqueous phase and CO_2 rich phase (supercritical/liquid/gas)
2. Reactivity of cement : CO2 brine (pH=3), cement pore solution (pH=13)
3. Interface behavior: coupling of 1. and 2.

→ *Need for a coupled geochemical transport model*

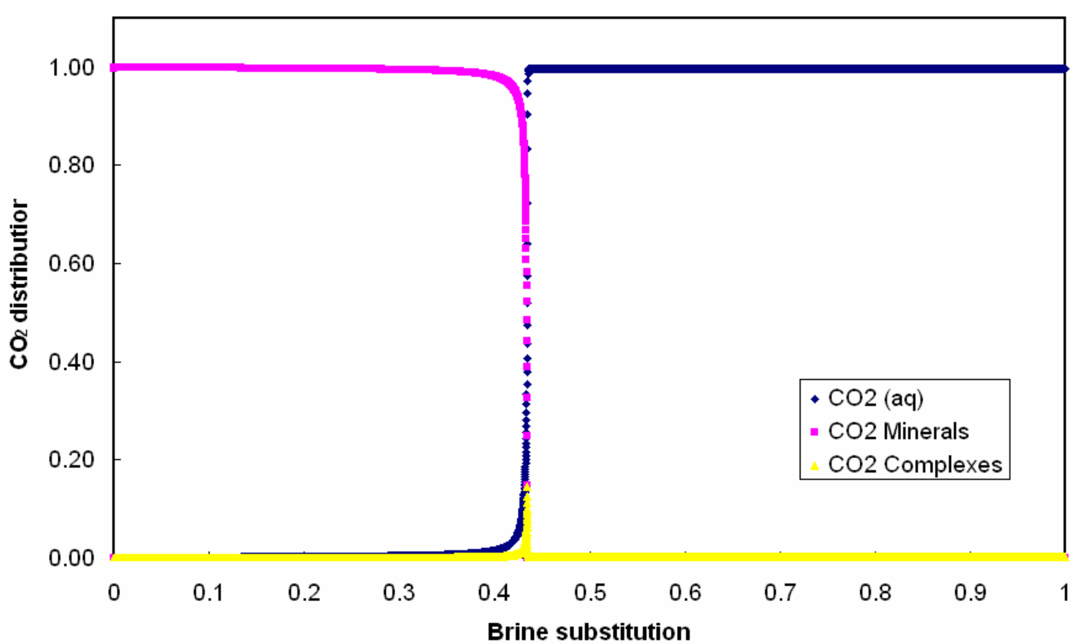
Chemistry approach

Batch experiments simulation:

→ Flush of cement with CO2 saturated sea water.

✓ Cement = Portlandite + Jennite + Ettringite + Monosulfoaluminate + dissolved NaOH (0.25M)

✓ Brine = NaCl (0.5 M), CO_2 (1 bar)



Reactive Transport of Ions in Cement-Based Porous Material [1]:

1. Transport of aqueous species (for each ion):

$$\frac{\partial(\theta c_i)}{\partial t} = \theta D_{e,i} \frac{\partial^2 c_i}{\partial x^2} \qquad i \in \{1, N_{sp}\}$$

I. Diffusion

$$+ \quad \theta D_{e,i} \left(\frac{\partial c_i}{\partial x} \frac{\partial \ln \gamma_i}{\partial x} + c_i \frac{\partial^2 \ln \gamma_i}{\partial x^2} \right)$$

II. Electrical coupling

$$+ \quad \theta D_{e,i} \frac{z_i F}{RT} \left(\frac{\partial c_i}{\partial x} \frac{\partial \psi}{\partial x} + c_i \frac{\partial^2 \psi}{\partial x^2} \right)$$

III. Activity correction

$$+ \quad \left(\frac{\partial c_i}{\partial x} + c_i \frac{\partial \ln \gamma_i}{\partial x} + c_i \frac{z_i F}{RT} \frac{\partial \psi}{\partial x} \right) \frac{\partial(\theta D_{e,i})}{\partial \theta} \frac{\partial \theta}{\partial x}$$

IV. Porosity correction

2. Local equilibrium:

Heterogeneous reactions: e.g. $Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2\,OH^-$

$$\sum_{j=1}^{N_c} \nu_{ij} \left(Log(\gamma_j) + Log\left(C_j^0 + \sum_{k=1}^{M} \nu_{jk} \, \Delta S_k \right) \right) + Log(K_{fi}) = 0 \quad , i \in \{1, M\}$$

[1]: E. Samson and J. Marchand, Université Laval, Québec, Canada G1K 7P4

Reactive Transport of Ions in Cement-Based Porous Material:

1. Numerical method:

   SNIA: Sequential Non Iterative Approach

2. Assumption:

   - local thermodynamic equilibrium
   - pure diffusion process

3. Choice of time step Δt and space step Δx for simulations:

- Critical time: Reaction $t_R = \dfrac{1}{(k_e S_a)}$

  Diffusion $t_D = \dfrac{L^2}{D_e}$

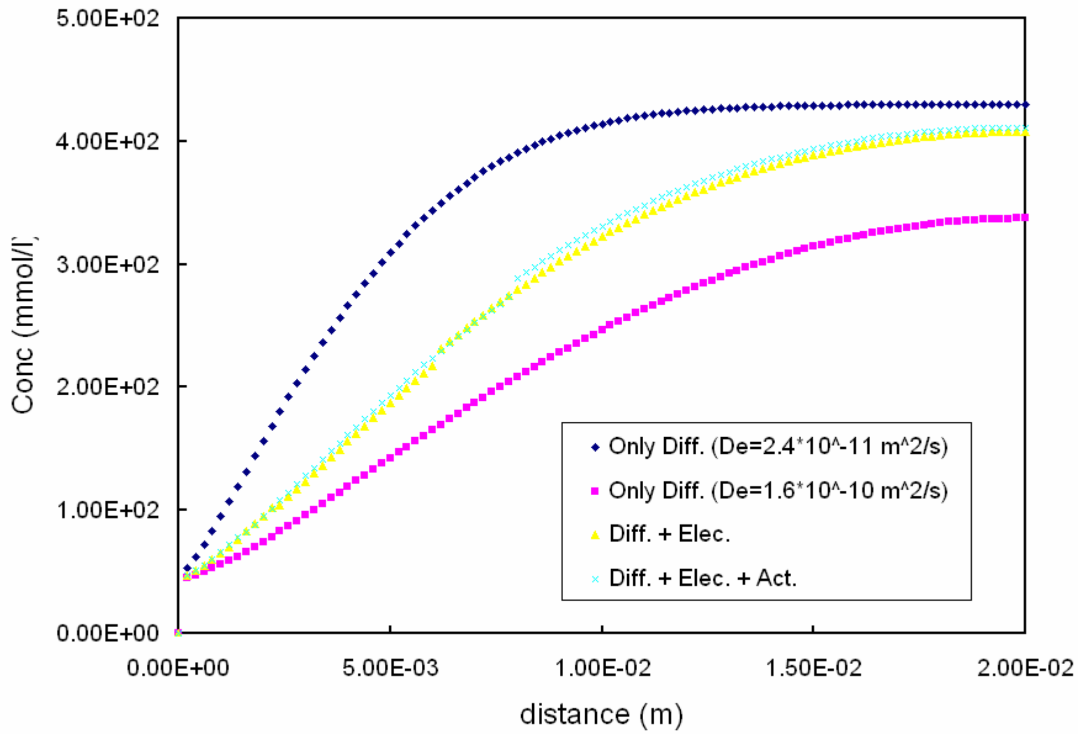
- time step $t_r \prec \Delta t \prec t_D$

- space step $\Delta x \succ \sqrt{\dfrac{D_e}{k_e S_a}}$

Cement chemical behavior in pure de-ionized water

Concentration profile (after 6 days):

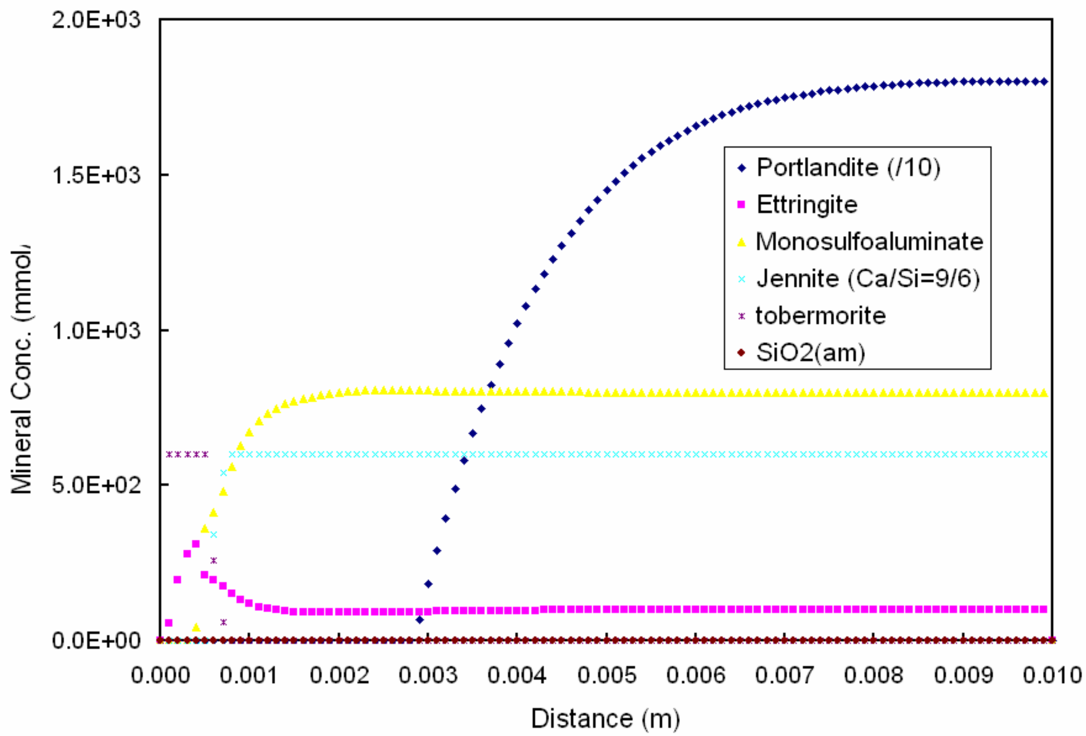
Importance of various terms of the transport equation



Cement chemical behavior in pure de-ionized water

Mineral profile (after 6 days):

Input parameters: $D_e = 10^{-11}$ m^2/s, $\phi = 0.5$, $dx = 10^{-4}$m, $dt = 10^3$s, L=1cm

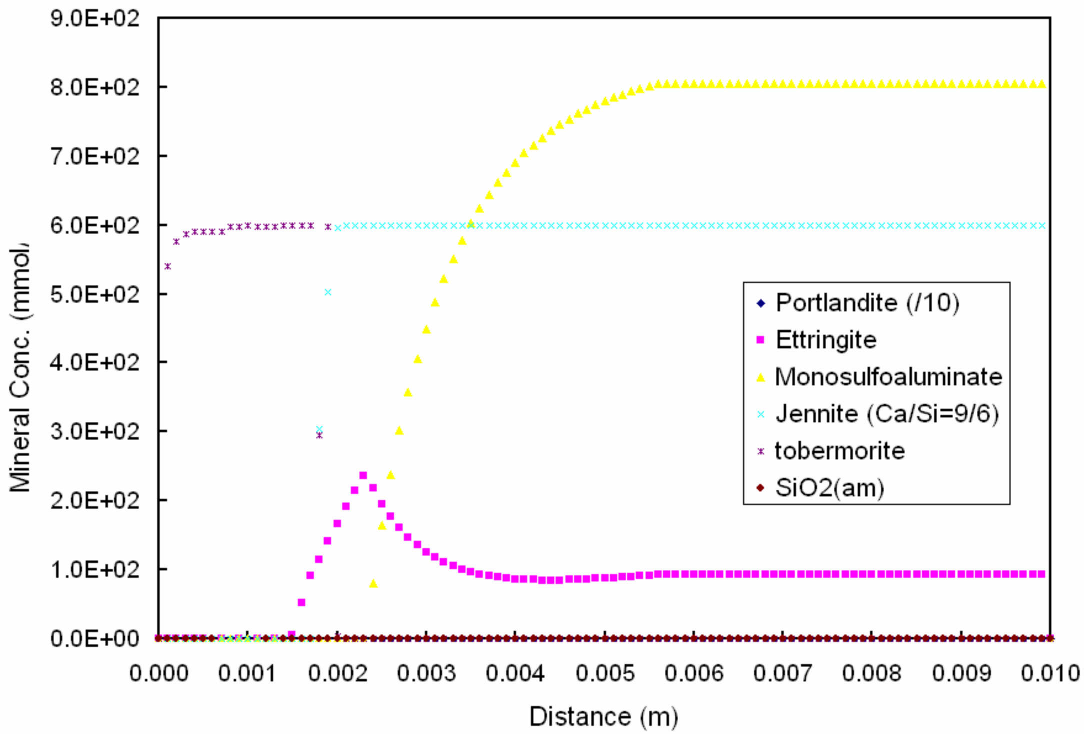


Mineral zoning:

1. Portlandite, Jennite, Aft. AFm
2. Jennite, Aft, AFm
3. Tobermorite, Aft

Cement chemical behavior in pure de-ionized water

Mineral profile (after 1 month):



Portlandite dissolved throughout the 1 cm cement sample after 1 month

Key parameters: microstructure (tortuosity, porosity) and
buffer capacity (calcium content, hydrates reactivity)

Current and Future Work

- Integrating aqueous chemistry
- Temperature
- Improved description of C-S-H (logK = f (Ca/Si)
- Reaction Kinetics (needed for CSH with low Ca/Si ratio)

- 2D – simulations of CO_2 multiphase transport up the wellbores:
  1. Modeling of segments of wellbores
  2. Modeling the dynamic behavior of defects (widening, self healing, cracks opening)